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THE TEMPERATURE DEPENDENCE OF TRIPLET STATE REACTION RATE AND

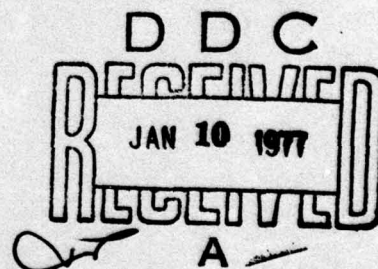# QUANTUM YIELD FOR AN INTRAMOLECULAR ENONE PHOTOCYCLOADDITION

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Valence photoisomerization (320-380 nm) of endo-tricyclo$(5.2.1.0^{2,6})$deca-4,8-diene-3-one has been studied as a function of temperature. At 4 - 51 the isomerization quantum yield is independent of temperature (ϕ = 0.4). In the same range the lifetime for the triplet state responsible for isomerization decreases. Arrhenius parameters for triplet decay are computed: E_a = 4.7kcal/mol; log A = 13.7. A mechanism involving formation of a diradical intermediate which partitions to the valence isomers is suggested.

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THE TEMPERATURE DEPENDENCE OF TRIPLET STATE REACTION RATE AND QUANTUM YIELD FOR AN INTRAMOLECULAR ENONE PHOTOCYCLOADDITION.

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Although photochemically induced rearrangements of ketones have been the focus of numerous studies,[1] few reports have documented a temperature dependence of excited state reaction rates or of quantum yields.[2] We wish to provide Arrhenius parameters for reactive decay of an excited enone. Our study of the kinetics of valence isomerization $1 \rightarrow 2$ is the first detailed look at an intramolecular version of cyclopentenone photoannelation,[3] and is of additional interest since the $1 - 2$ couple is a prototype photon energy storage system.[4] We note particularly that the high rate of reaction of triplet 1 is moderately temperature dependent while the quantum yield for isomerization is not.

Isomerization $1 \rightarrow 2$ is clean, quantum-efficient, highly endoergic, moderately photochromic, and reversible upon treatment at elevated temperatures with Rh(I) catalysts.[4] The reaction may be sensitized as shown in Table I. The effectiveness of acetophenone vs. anthrone is consistent with a triplet energy for 1, $E_T = 72.9$ kcal/mol, estimated from its emission at 77°K in EPA glass (λ_{max} 392 nm, 1680 cm^{-1} vibrational spacing).[6] The results also point to a unit quantum efficiency for intersystem crossing which precedes photorearrangement on direct irradiation of 1.

Isomerization was quenched by 2,5-dimethyl-2,4-hexadiene ($E_T < 58$ kcal/mol), and plots of ϕ_o/ϕ vs. [Q] were linear. The results of Stern-Volmer analysis along with quantum yields and rate constants for diffusion controlled quenching by diene (k_q) for different temperatures are shown in Table II.

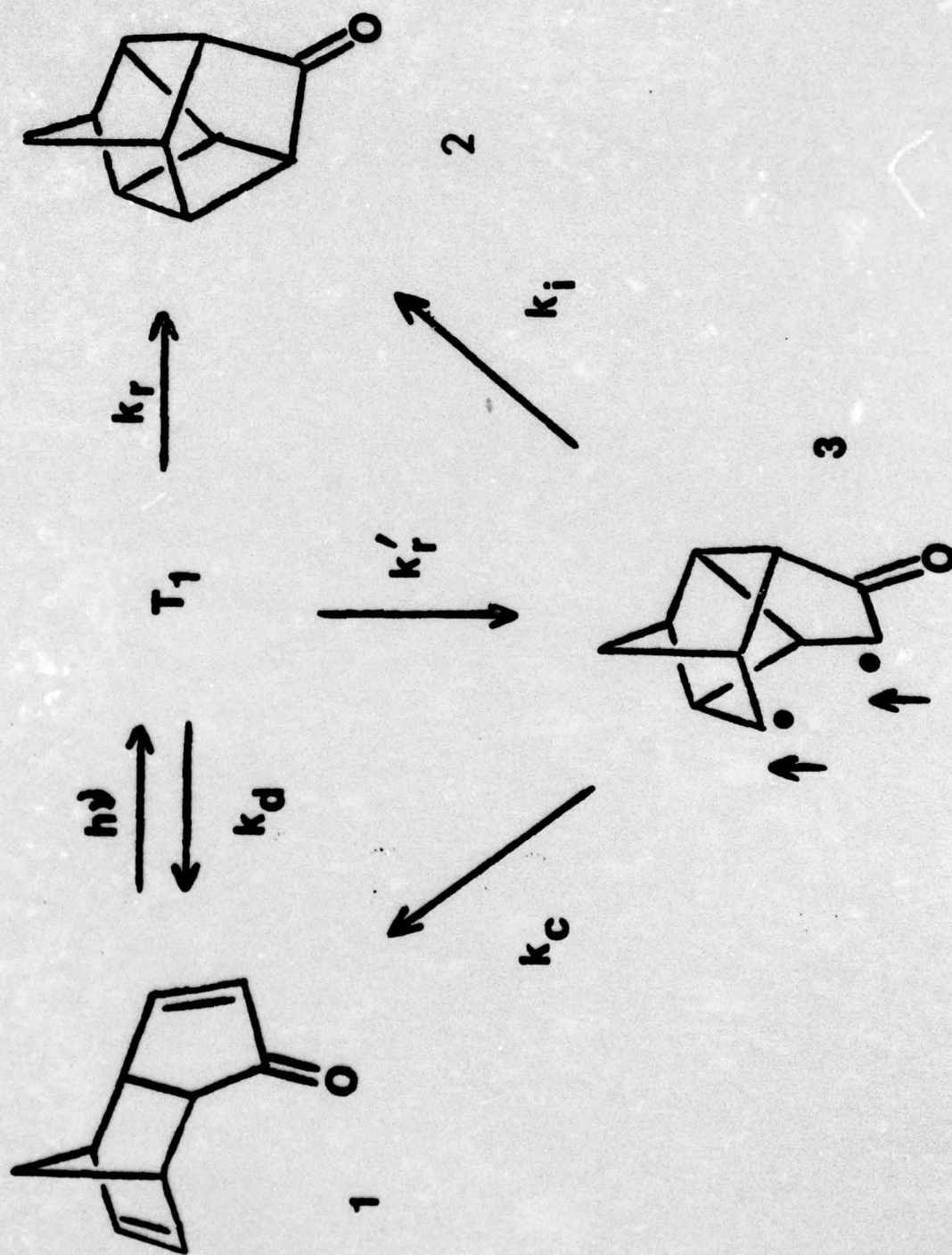Assuming a mechanism for photoisomerization in which T_1 partitions with inter-

Table I. Quantum Yields for Sensitized Isomerization $\underset{\sim}{1} \rightarrow \underset{\sim}{2}$[a]

Sensitizer (M)[b]	E_T (kcal/mol)	ϕ[c]
---	---	0.37 ± 0.02
acetophenone (0.3)	73.6	0.33 ± 0.02
anthrone (0.07)	71.9	0.06 ± 0.004

[a] Rayonet reaction, 3500 lamps (325 - 385 nm), valerophenone actinometer (ref 5), 0.07 M $\underset{\sim}{1}$ in benzene. [b] > 80% light absorbed by sensitizer. [c] Corrected for competative and differential absorption.

system crossing directly to $\underset{\sim}{2}$ (k_r) and to $\underset{\sim}{1}$ (k_d), one applies the relationships, $\phi_o/\phi = 1 + k_q[Q]/k_r + k_d$ and $\phi_o = k_r/k_r + k_d$ and finds that (at 30°), $k_r = 8.0 \times 10^9$ sec^{-1} and $k_d = 1.4 \times 10^{10}$ sec^{-1}. The calculated k_d is unacceptable in view of the size of radiationless decay constants determined for other enones ($k_d = 10^7 - 10^8$ sec^{-1}).[3a] Treatment of the data using the Arrhenius equation gives the preexponential factors, log A $\sim$ 13, for both k_r and k_d. These values appear improbably high for intercombinational processes.

In an alternative scheme, T_1 does not lead directly to $\underset{\sim}{1}$ or $\underset{\sim}{2}$ but gives triplet diradial $\underset{\sim}{3}$,[7] which partitions to the isomers. The relationship, $\phi_o/\phi = 1 + k_q[Q]/k_r'$, then applies, with which k_r' may be obtained (results shown in Table II). An Arrhenius plot of the rate data is shown in the Figure along with calculated parameters for k_r'.

For the diradical mechanism, absolute quantum yields for photorearrangement are determined by the relative rates of closure (k_i) and cleavage (k_c) of $\underset{\sim}{3}$, and $(1/\phi_o) - 1 = k_c/k_i$. A plot of $(1/\phi_o) - 1$ vs. $1/T$ shows that $E_a (c) - E_a (i) = 0.09 \pm 0.17$ kcal/mol and $A (c) / A (i) = 2.0 \pm 0.6$.

The quantum yield for photoisomerization is understood then in terms of frequency

Table II. Direct Irradiation Quantum Yields and Quenching Data for Isomerization

$\mathcal{l} \rightarrow \mathcal{l}$

$T(°C)^a$	$\emptyset$	Slope $(M^{-1})^b$	k_q $(M^{-1}\ sec^{-1})^c$ $\times 10^{-9}$	k_r' (sec^{-1}) $\times 10^{-10}$
4	---	0.395 ± 0.025	4.15	1.05 ± 0.07
18	0.38 ± 0.02	0.345 ± 0.015	5.38	1.56 ± 0.07
30	0.37 ± 0.02	0.310 ± 0.015	6.72	2.17 ± 0.11
40	0.36 ± 0.02	0.275 ± 0.015	7.84	2.85 ± 0.15
51	0.38 ± 0.02	0.265 ± 0.015	9.33	3.52 ± 0.20

[a] ± 1°C. [b] From plots of $\emptyset_o/\emptyset$ vs. [Q]; irradiation at 325-385 nm in cyclooctane solution. [c] Calculated using the Debye equation and measured viscosities.

factor differences favoring diradical cleavage over closure.[6][ff] The diradical mechanism is economical, it leads to an informative treatment of the quantum yield and quenching data, but it is not uniquely consistent with the facts.[8] We will discuss in a full paper the possibilities that the thermal barrier to photoisomerization separates an initial enone triplet from a reactive (unquenchable) upper triplet of different configuration or from a conformation which is equivalent to the exciplex in intermolecular photoannelation[3a] (in which enone and olefin chromophores interact strongly)[10].
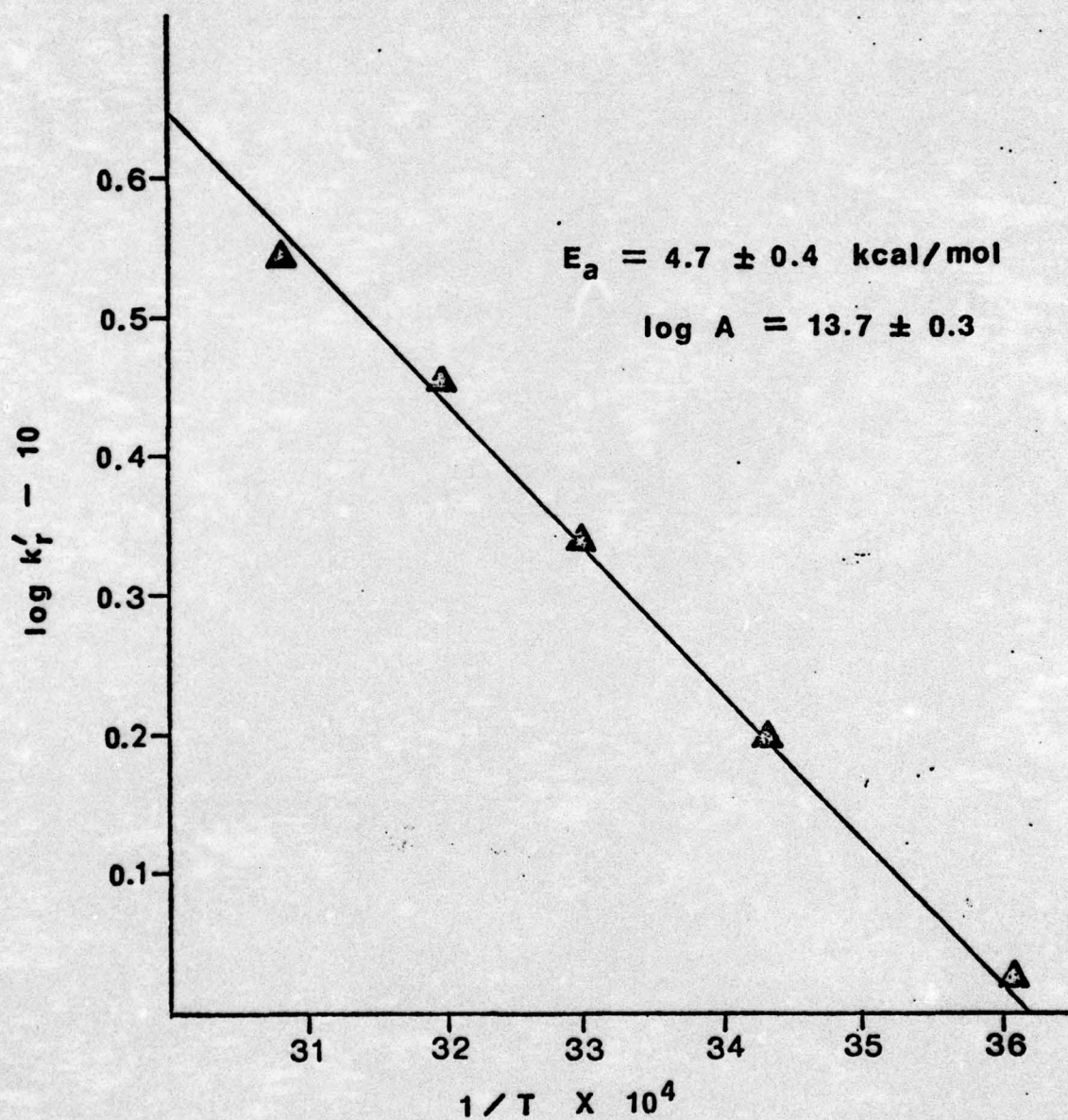
Figure. Arrhenius plot and parameters, indicating the temperature dependence for reactive decay of triplet $\underset{\sim}{1}$ (k_r').

(1) See, for example, (a) S.S. Hixson, P.S. Mariano, and H.E. Zimmerman, Chem. Rev., 73, 531 (1973); (b) K. Schaffner in "Organic Reactions in Steroid Chemistry," vol 2, Ed., J. Fried and J.A. Edwards, Van Nostrand Reinhold Co., N.Y., 1972, p 288; (c) H.E. Zimmerman, Angew. Chem. Intern. Ed. Engl., 8, 1 (1969).

(2) (a) H.E. Zimmerman and W.R. Elser, J. Amer. Chem. Soc., 91, 887 (1969); (b) C.D. DeBoer, W.G. Herkstroeter, A.P. Marchetti, A.G. Schultz, and R.H. Schlessinger, ibid., 95, 3963 (1973)

(3) (a) P. de Mayo, Accounts Chem. Res., 4, 41, (1971); (b) P.E. Eaton, ibid., 1, 50 (1968); (c) P.G. Bauslaugh, Synthesis, 2, 287 (1970)

(4) G. Jones, II and B.R. Ramachandran, J. Org. Chem., in press.

(5) P.J. Wagner, P.A. Kelso, and R.G. Zepp, J. Amer. Chem. Soc., 94, 7480 (1972).

(6) Sensitization of isomerization $\underline{1} \rightarrow \underline{2}$ by the T_2 state of substituted anthracenes ($E_{T_2} \sim$ 73 - 74 kcal/mol) has been reported; see R.O. Campbell and R.S.H. Liu, J. Amer. Chem. Soc., 95, 6560 (1973), and R.S.H. Liu and J.R. Edman ibid., 91, 1492 (1969).

(7) (a) For a summary of mechanistic possibilities for enone photoannelation including the diradical route, see ref 3a. (b) We have chosen for illustration the more stable diradical with no experimental basis for excluding intervention of its regioisomer.

(8) For intermolecular photoannelation direct formation of diradical from triplet enone (plus olefin), without intervention of an exciplex has been considered doubtful due to the high rates of addition (k_r's $\sim 10^8 - 10^9$ M^{-1} sec^{-1}) compared to the bimolecular rates of olefin - radical reactions.[3a] The free radical, ground state model may be unsatisfactory however, in view of the likely greater exothermicity of photoaddition and if the enone triplet utilizes a pyramidal[9] reactive center (odd e density in a directed orbital), for attack on olefin. For 1, we also expect an especially high rate of intramolecular triplet enone addition, enhanced by a high frequency factor (by comparison, much more favorable entropy of activation) as observed.

(9) K. Wiesner, Tetrahedron, 31, 1655 (1975).

(10) Although enone and olefin chromophores (according to models) are separated by only 2.5 - 3.0 Å, there is no indication in the uv absorption or low temperature emission spectra of significant interaction in the ground state or lowest triplet equilibrium geometries.